Mass Spectra of Nitrones. Electron Impact Mass Spectra of Fluorenone Nitrones

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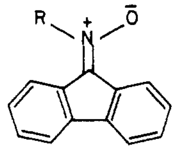
N-Methyl and N-aryl α,α-(biphenyl-2,2′-diyl)nitrones, 1a–e, have been examined by mass spectrometry. Metastable ion kinetic energy spectra (IKES) recorded by using the accelerating voltage scan method afforded valuable information regarding the correct fragmentation mode of these substances. This technique has been used for the first time in the nitrone series. Exact mass measurements permitted the assignment of various ions. New decomposition pathways are suggested.

Introduction

The electron-impact fragmentation patterns of many nitrones have been examined (*1–4*, *6*). In most cases, nitrogen was substituted with either alkyl or aryl groups, and the α carbons were substituted with either phenyl or substituted phenyl groups. C,C-Diphenyl N-benzyl nitrone has also been investigated by other workers (*5*).

Therefore, it appeared of interest to examine the mass-spectral fragmentation of N-methyl and N-aryl α,α-(biphenyl-2,2′-diyl)nitrones (**1a–e**) and compare these results with those obtained for α,α-diphenyl N-substituted nitrones in order to ascertain the effect of the α,α-diphenyl-2,2′-diyl function, which could introduce certain modification in the fragmentation mode. To our knowledge, mass-spectral studies of such nitrones have not been previously carried out. The syntheses of **1a** (*7*) and **1b–e** (*8*) have been reported recently.



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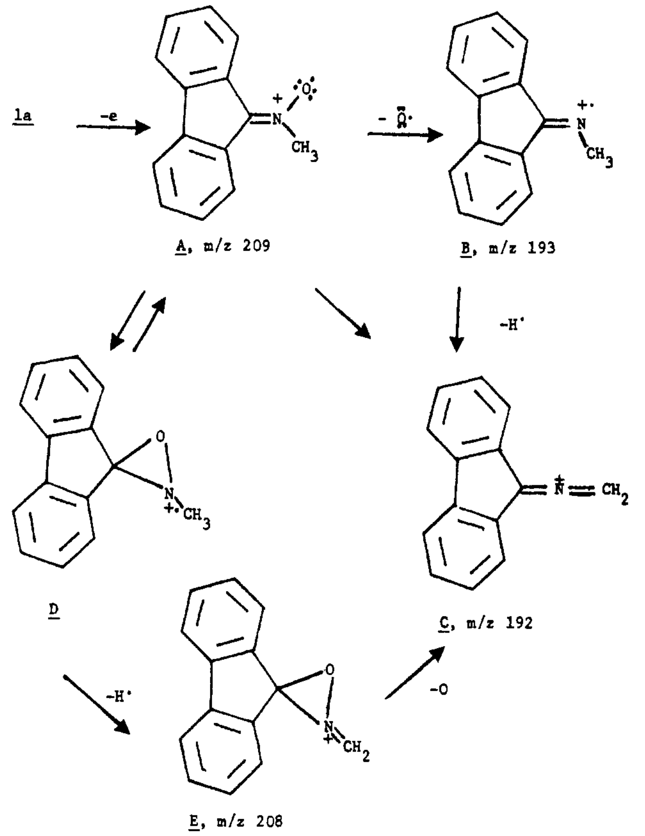
a, R = CH_3
b, R = CH_2Ph
c, R = p-CH_3Ph
d, R = p-CH_3OPh
e, R = p-FPh

The present investigation deals with the results obtained by electron impact on five nitrones **1a–e**. Metastable ion kinetic energy spectra (IKES) have been employed to determine the correct decomposition mode of various ions. Exact mass measurements afforded the elemental composition. IKES have been employed for the first time in the nitrone series. The results are described below.

Results and Discussion

Nitrone 1a. Compound **1a** on electron impact provided $M^{+\cdot}$. The ^{13}C satellite peak at *m/z* 210 (Figure 1) clearly indicated the presence of 14 carbon atoms in the molecule. Species A (see Scheme I) loses an atomic oxygen to give Schiff base B at *m/z* 193, which ejects a hydrogen radical to provide C at *m/z* 192. IKES showed that fragment C is formed mainly from B but also to a small extent from the precursor ions A (*m/z* 209) and E (*m/z* 208). The elemental composition of C was obtained by exact mass measurement (calcd, 192.0813; found, 192.0814).

Scheme I



Fragment D loses CH_3–N̈· to produce a daughter ion F, at *m/z* 180. This path is supported by IKES. High-resolution work confirmed this assumption. Ejection of a hydrogen radical from F affords fragment G, and this is the major fragmentation path (Scheme II). However, IKES results showed that G (*m/z* 179) is also produced to a very small extent from ions 209, 208, and 194. Furthermore, the high-resolution spectrum of **1a** (resolving power of 8000) gave a value of 179.0757 for the mass of the peak at *m/z* 179, confirming the presence of ion H (calcd, 179.0735) in addition to ion G (calcd, 179.0497).

Since formation of ion I (*m/z* 152) from C involves the conversion of an even electron ion going to an odd-electron ion, this process is not favorable and explains why this path contributes only to a very small extent. Initially, we thought that ion J (*m/z* 151) might have originated only from the species I. However, in an attempt to confirm this by IKES using K, we found that K as well as I are the precursor ions for this fragment: K provides ~70% and I ~30% of ion J.

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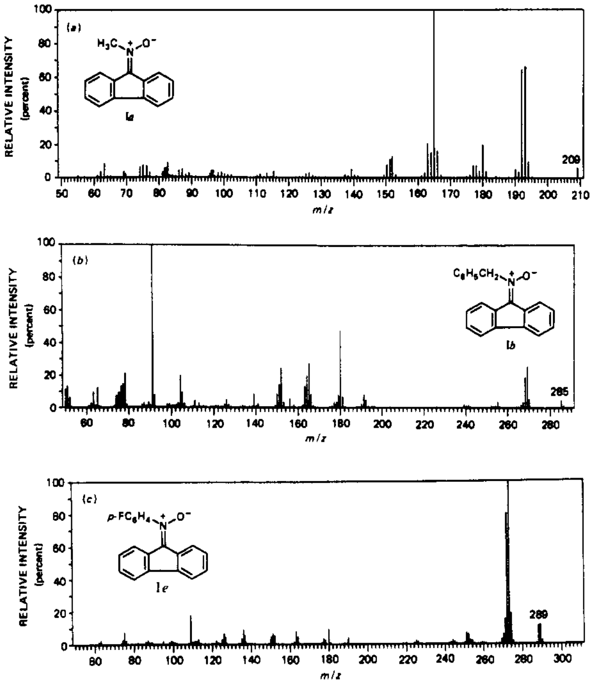
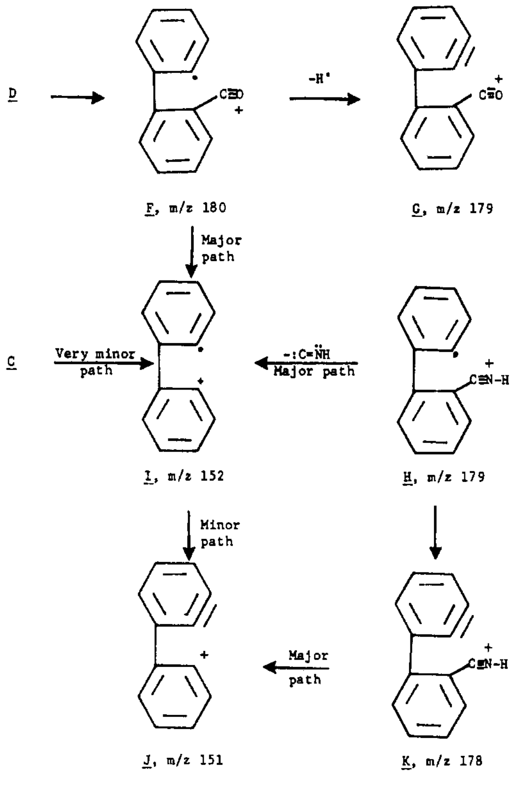


Figure 1.

Scheme II

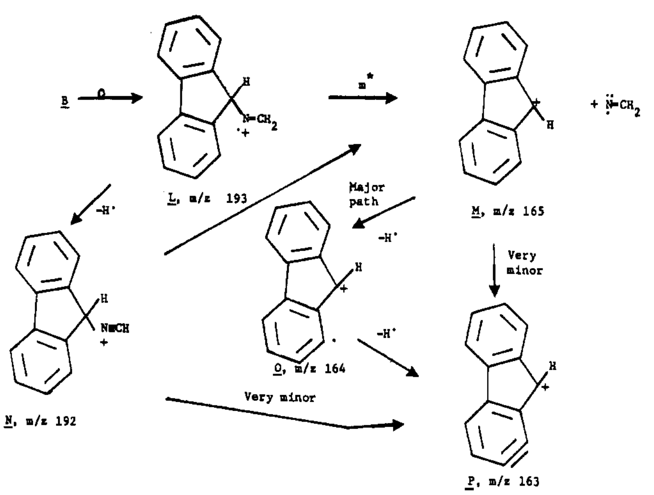


The ion B rearranges to L (*m/z* 193) and then ejects a species $CH_2{=}\ddot{N}\cdot$ to give the fragment of mass 165 (*m**). This is the base peak in the spectrum. It is interesting to observe that M is formed equally well from both ions L (*m/z* 193) and N (*m/z* 192). This path was confirmed through IKES. A proposed mechanism for the formation of fragment M from ions L and N is shown in Scheme III.

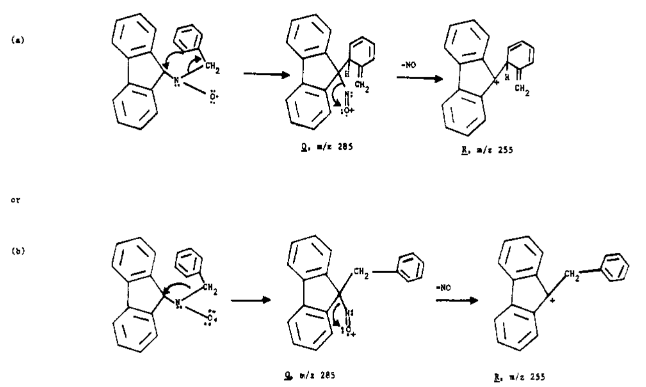
It is noteworthy that species O (*m/z* 164) originates almost entirely from the precursor ion M (*m/z* 165) because this process again is unfavorable and involves spin unpairing in order to lose a hydrogen radical.

Nitrone 1b. We next examined compound **1b** to see the effect of substituting the hydrogen of the methyl group of **1a** by a phenyl group. The base peak was at *m/z* 91, which represents a benzyl or tropylium ion. The other ion is due to $C_7H_7N^{+}\cdot$ at 105. The most interesting fragment was R (*m/z* 255). This fragment arises from the migration of the benzyl function to the α carbon of nitrone followed by the loss of NO, as shown in Scheme IV (*5*).

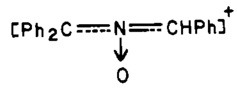
Scheme III



Scheme IV



Neiman and collaborators (*6*) reported that $M^{+}\cdot$ of *C*,*C*-diphenyl *N*-benzyl nitrone eliminates a hydrogen atom to form an ambident ion

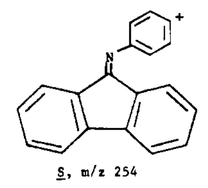


$$[Ph_2C\overset{\dots}{=}N\overset{\dots}{=}CHPh]^{+} \atop {\downarrow \atop O}$$

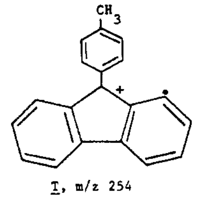
which can rearrange to two isomeric oxazirane ions, the first of which undergoes further breakdown to the benzophenone ion and the second to the benzaldehyde ion and benzoyl cation. In our study on *N*-benzyl α,α-(diphenyl-2,2′-diyl) nitrone **1b**, the $M^{+}\cdot - 1$ peak was of negligible intensity. Also, the fragment at *m/z* 105 was found to be due to $PhCH_2N^{+}\cdot$ by high-resolution work (calcd, 105.057 67; found, 105.056 60).

It is therefore, clear that **1b** does not produce a benzoyl ion. In other words, the formation of an ambident ion from **1b** was not observed.

Nitrone 1c. Compound **1c** first lost an oxygen atom followed by the ejection of a methyl group to give the fragment S (*m/z* 254). Again this was supported by IKES. Exact mass mea-

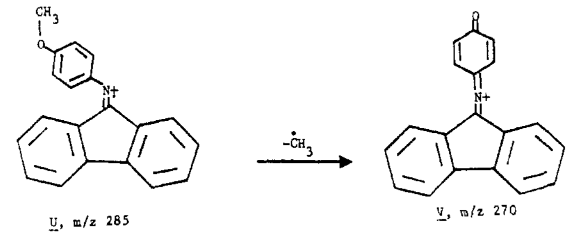


S, m/z 254

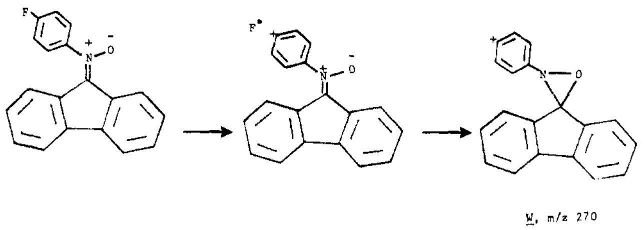


T, m/z 254

Scheme V



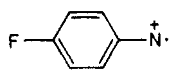
Scheme VI



surements showed that ion T (*m*/*z* 254) is not formed, thereby eliminating the possible migration of a *p*-tolyl group to the α carbon.

Nitrone 1d. In the case of **1d**, it was possible to show that it is the Schiff base U (*m*/*z* 285) which provides V (*m*/*z* 270) (Scheme V). This was supported by a metastable transition for the process 285 → 270 + 15 (calcd, 255.78; found 255.80) observed in the low-resolution spectrum. This was further confirmed by IKES.

Nitrone 1e. The electron-impact effect on **1e** was also interesting. The base peak was at *m*/*z* 273 due to loss of oxygen atom (Table I). The peak $M^+ - OH$ was also intense. Loss of the fluorine atom was also observed to a small extent. The probable structure of the fragment at *m*/*z* 270 is W (Scheme VI). Formation of an ion at *m*/*z* 109



was observed, having an intensity of 23.1%.

Conclusion

The above results clearly demonstrate that the substituents on nitrogen exert a considerable influence on the nitrone system, and in the present study significant differences have been observed in the fragmentation patterns of various N-substituted nitrones. The fragmentation of **1b**, unlike other *N*-benzyl nitrones (*5*), exhibited a $M^+ - 1$ peak of negligible intensity. Furthermore, high-resolution mass measurements of the peak at *m*/*z* 105 showed the absence of benzoyl ion.

Experimental Section

Low- and high-resolution mass spectra were obtained on a Hitachi-Perkin-Elmer RMH-2 mass spectrometer. A resolution of 6500 was employed for the exact mass measurements except for one ion (*m*/*z* 179 of compound **1a**) where a resolution of 8000 could be achieved. The computer, a Data General Nova 2, using the Kratos AE1 DS-50 data system, was employed. Ionizing energy in all cases was 70–80 eV. The samples were introduced through a direct insertion probe while maintaining the sample temperature around 25–50 °C. The chamber temperature was ~100 °C.

Analyses of the metastable ions were carried out by varying the accelerating voltage (up to a maximum of 10 200 V). Each time, the magnetic field of daughter ion was first fixed at a value appropriate to the ESA voltage being used. The accelerating voltage was then increased in order to detect the metastable peak(s) of the precursor ion(s) formed in the first field free region.

Table I. Relative Abundance of Nitrones

R = CH_3		R = CH_2Ph		*p*-CH_3Ph		*p*-CH_3OPh		*p*-FPh	
m/*z*	RA	*m*/*z*	RA	*m*/*z*	RA	*m*/*z*	RA	*m*/*z*	RA
209	6.1	285	4.5	285	10.4	301	6.8	289	15.6
208		284	0.1	284	5.8	300	5.7	288	14.2
194	9.7					286	13.9		
193	66.5	269	25.3	269	100.0	285	54.3	273	100.0
192	64.6	268	18.8	268	48.0	284	0.6	272	80.0
191	3.6	267	3.5			283	0.6	271	15.4
		255	3.4	255	3.8	271	23.4	270	5.7
		254	0.9	254	17.1	270	100.0	254	2.3
		253	0.8	253	6.5	269	1.3	253	2.2
		241		241	2.34	241	27.0		
						240	12.4		
180	19.9	180	43.3	180	22.2	180	5.1	180	8.7
179	4.1	179	7.6	179	1.1	179	1.5	179	0.5
178	7.4	178	3.2	178	2.6	178	4.5	178	3.2
177	7.1	177	3.2	177	4.3	177	1.7	177	4.1
165	100.0	165	27.1	165	3.0	165	9.20	165	0.7
164	15.3	164	19.6	164	7.3	164	4.4	164	4.9
163	20.6	163	13.0	163	13.2	163	9.4	163	9.9
152	12.7	152	24.4	152	8.7	152	3.9	152	6.6
151	11.2	151	14.3	151	8.0	151	3.9	151	8.2
		105	9.2	105	47.1	121	5.9	109	23.1
		104	19.4	104	11.9	120	8.2	108	1.5
		91	100.0	91	7.0	91	1.5	95	3.4
78		78	21.0	78	12.1	78	1.0		
77	3.0	77	14.3	77	7.6	77	2.7	77	1.1

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